

What is claimed is:

1. A method for making a fabric having a laundry-durable finish by excitation-induced graft polymerisation of a polymerisable monomer, the method comprising:
 - a) exposing the fabric or a region thereof to polymerisable monomer, and
 - b) exciting the polymerisable monomer within a monomer excitation zone,
 and wherein the polymerisable polymer and the exposure and excitation conditions are such that the resulting polymer-coated fabric or region thereof has an average fibre-coating thickness of from about 1.5 to about 25 nm, a coating abrasion resistance of at least about 1000 rubs (Martindale Abrasion Test, ISO 12947-2, 12kPa load, 50% minimum finishing performance) and wherein the polymer is graft-polymerised substantially wholly on or in the individual fabric fibres with substantially no coalescence of fibre bundles whereby the air permeability of the fabric or region thereof after treatment is within about $\pm 20\%$ of that of the untreated fabric.
2. The method of claim 1 wherein the fabric or region thereof has an average fibre-coating thickness of from about 2.5 to about 20 nm, a coating abrasion resistance of at least about 3000 rubs and wherein the air permeability of the fabric or region thereof after treatment is within about $\pm 15\%$ of that of the untreated fabric.
3. The method of claim 2 wherein the fabric or region thereof has an average fibre-coating thickness of from about 3 to about 15 nm, a coating abrasion resistance of at least about 3000 rubs and wherein the air permeability of the fabric or region thereof after treatment is within about $\pm 10\%$ of that of the untreated fabric.
4. The method of claim 1 wherein the polymerisable monomer is selected to impart one or more laundry-durable finishes selected from oleophobicity, hydrophobicity, stain repellency stain release, soil-resistance, soil release, malodor resistance, malodor release, crease resistance, softness, flame retardancy, color-bleeding resistance, dye-transfer inhibition and odor receptivity.
5. The method of claim 4 wherein the polymer-coated fabric or region thereof has an average hexadecane wetting hysteresis factor of less than about $\pm 30\%$, wherein the hexadecane wetting hysteresis factor is defined as $(\theta_a^{\text{hex}} - \theta_r^{\text{hex}}) / \theta_a^{\text{hex}}$, and θ_a^{hex} , θ_r^{hex} are respectively the advancing and receding contact angles for n-hexadecane on the polymer coated fabric or region thereof at 20°C.
6. The method of claim 5 wherein the fabric or region thereof has an average water wetting hysteresis factor of less than about $\pm 30\%$ wherein the water wetting hysteresis factor is defined as $(\theta_a^{\text{wat}} - \theta_r^{\text{wat}}) / \theta_a^{\text{wat}}$, and θ_a^{wat} , θ_r^{wat} are respectively the advancing and receding contact angles for deionised water on the polymer coated fabric or region thereof at 20°C.

7. The method according to claim 1 wherein the excitation zone is selected from radiofrequency- and microwave-generated plasma zones.
8. The method of claim 1 wherein the fabric is a natural or semi-natural woven fabric selected from cotton, silk, wool, linen, rayon and mixtures thereof as well as blends thereof with one or more synthetic polymers.
9. The method of claim 8 wherein the fabric is silk or a silk blend and wherein the polymerisable monomer is selected to impart a laundry-durable oleophobic finish to the fabric or region thereof.
10. The method of claim 1 wherein the excitation zone is a pulsed plasma having an on-time for unsaturated vapor-phase polymerisable monomers of from about $5\mu\text{s}$ to about $100\mu\text{s}$, an on-time for saturated polymerisable monomers of from about $40\mu\text{s}$ to about 2ms , an off-time of at least 1ms , a duty cycle in the range from about $\frac{1}{2}$ to about $1/10000$, and an average excitation power density in the range from about 10^{-7} to about 10^{-1} Watts/cm².
11. The method of claim 10 wherein the excitation zone is a sub-atmospheric vacuum pulsed plasma having an on-time for unsaturated vapor-phase polymerisable monomers of from about $20\mu\text{s}$ to about $70\mu\text{s}$, an on-time for saturated polymerisable monomers of from about $100\mu\text{s}$ to about 1ms , an off-time of from about 2ms to about 50ms , a duty cycle in the range from about $1/100$ to about $1/5000$ for unsaturated vapor-phase monomers and from about $1/4$ to about $1/300$ for saturated vapor-phase monomers, and an average excitation power density in the range from about 10^{-6} to about 10^{-2} Watts/cm².
12. The method of claim 1 wherein the polymerisable monomer is a saturated or unsaturated long-chain fluoro-substituted monomer containing an uninterrupted fluoroalkyl group of formula $\text{C}_n\text{X}_{2n+1}$ wherein each X is independently selected from the group consisting of halogen, H, and O-linked sidechain substituents, and wherein the fluoroalkyl group contains at least n fluoro substituents wherein n is in the range from about 5 to about 15, and wherein the fluoroalkyl group contains a linear fluorocarbon segment of at least 5 carbon atoms in length.
13. The method of claim 12 wherein the fluoroalkyl group contains at least $2n-3$ fluoro substituents, wherein n is in the range from about 6 to about 10.
14. The method of claim 12 wherein the polymerisable monomer has the general formula $[\text{C}_n\text{X}_{2n+1}\text{YTQ}]_m\text{R}$, wherein R is selected from the group consisting of C_1 - C_8 -alkyl and alkylene, C_3 - C_8 -cycloalkyl and cycloalkylene, C_2 - C_8 -heterocycloalkyl and heterocycloalkylene, C_2 - C_8 -

alkenyl and alkenylene, C₂-C₈-alkynyl and alkynylene, and C₄-C₈-alkadienyl and alkadienylene, each said R group being optionally substituted with one or more halogen atoms; m is from 1 to 3; T represents the moiety (C(R¹)₂)_p wherein each R¹ is independently selected from the group consisting of H, halogen, hydroxy, C₁-C₄ alkyl, hydroxy-substituted C₁-C₄ alkyl, halo-substituted C₁-C₄ alkyl, and mono- and poly-C₁-C₄-alkylene oxide moieties and wherein p is from 0 to 10; each Q independently represents a direct bond or a linking moiety selected from the group consisting of O, (C=O), O(C=O), (C=O)O, NR², NR²(C=O), (C=O)NR², O(C=O)NR² and (R²)₂Si, wherein, each R² independently selected from C₁-C₄ alkyl and halo-substituted C₁-C₄ alkyl groups; and Y is a direct bond or a sulphonamide group provided that when Y is a sulphonamide group, the corresponding T moiety has a p value of at least 1.

15. The method of claim 14 wherein the terminal carbon of the fluoroalkyl group or of T, if present, is free of H substituents when the corresponding group is directly connected to a Q linking moiety; and wherein the polymerisable monomer is perfluorinated when the monomer is free of Q linking moieties.
16. The method of claim 15 wherein the terminal carbon of the fluoroalkyl group or of T, if present, is substituted with two atoms or groups selected from the group consisting of halogens, C₁-C₄ alkyl and halo-substituted C₁-C₄ alkyl moieties, C₁-C₄-alkylene oxide and poly-C₁-C₄-alkylene oxide moieties having from 2 to 20 alkylene oxide moieties in the polymer chain, and combinations thereof.
17. The method of claim 14 wherein the polymerisable monomer has a rate constant for alkaline hydrolysis at pH 8 and above of less than about 1 x 10⁻⁵ L/mol-sec.
18. The method of claim 14 wherein the fabric as made has a surface F:C ratio as determined by XPS of at least about 1.25.
19. The method of claim 1 wherein the polymerisable monomer is of low or intermediate volatility with a boiling point in the range from about -50°C to about 150°C at 8000mTorr (10.7mbar).
20. The method of claim 1 including a plurality of excitation zones and wherein the fabric or one or more regions thereof is subjected to different excitation conditions within different excitation zones, the different excitation conditions being selected from the group consisting of different duty cycles, electrode temperatures, power parameters, pressure conditions, and electromagnetic phase characteristics.

21. The method of claim 20 wherein the fabric or region thereof is subjected in a first or earlier excitation zone to continuous or pulsed excitation under long duty cycle conditions to promote cross-linking and adhesion of the polymer in regions proximal to the surface of the fabric fibres and is thereafter subjected in a subsequent excitation zone to pulsed excitation under short duty cycle conditions to reduce cross-linking and fragmentation of the polymer in regions distal to the surface of the fabric fibres.
22. The method of claim 20 including both a plurality of excitation zones and a plurality of feed zones adapted to deliver one or more polymerisable monomers and/or one or more reactive or non-reactive gases to one or more regions of the fabric
23. The method of claim 1 wherein the fabric is a natural or semi-natural yarn-based woven fabric and wherein the method includes the step of drying the substrate to a moisture regain of (at 21°C, 65% RH) of at least about 5% prior to exposing the fabric to the polymerisable monomer.
24. A fabric having a laundry-durable finish made by graft polymerisation of a polymerisable monomer, the polymer-coated fabric or region thereof having an average fibre-coating thickness of from about 1.5 to about 25 nm and a coating abrasion resistance of at least about 1000 rubs (Martindale Abrasion Test, ISO 12947-2, 12kPa load, 50% minimum finishing performance), the polymer being graft-polymerised substantially wholly on or in the individual fabric fibres with substantially no coalescence of fibre bundles whereby the air permeability of the fabric or region thereof after treatment is within about $\pm 20\%$ of that of the untreated fabric.
25. A fabric according to claim 24 made by the steps of exposing the fabric or a region thereof to polymerisable monomer, and exciting the polymerisable monomer within a monomer excitation zone.